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OPTIMIZATION OF HPLC CONDITIONS TO ANALYZE WIDELY DISTRIBUTED ETHOXYLATED ALKYLPHENOL SURFACTANTS

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ABSTRACT

Commercial ethoxylated alkylphenol surfactants are always a mixture of oligomers with different ethylene oxide number (EON). The different oligomers can be separated by various HPLC techniques. Isocratic mode with mixed solvent on silica column allows to separate oligomers up to EON = 10; gradient programming moves the limit up to EON = 15. For higher EON values (up to 25) a NH₂ column has to be used, either with isocratic or gradient mode. Applications to the analysis of microemulsion systems and to the separation of tributyl phenol ethoxylates are discussed. Extreme separation of wide range EON distribution is attained with two columns (Si and NH₂) in series, and a solvent programming.

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INTRODUCTION

The polyethoxylated alkylphenols have held a prominent position in the field of nonionic surfactants in the past forty years. They are used in household products such as liquid dish washing formulations and hard surface cleaners, cleansers for textiles, leather, and plastics, particularly in systems with high electrolyte content. They are used extensively in the oil industry, e. g., as emulsifiers in drilling fluids and heavy crude emulsions (1), and have been proposed as tension-lowering surfactants for enhanced oil recovery (2-3).

Nonylphenol is by far the most widely used base material, followed by the octyl, dodecyl, and *n,n*-dinonyl counterparts; recently tri-butyl phenol ethoxylates have been also available.

Since the addition of ethylene oxide to an alkylphenol is a polycondensation process, the final product is not a pure substance, but rather a mixture of homologues with different ethylene oxide number (EON), so-called oligomers (4).

As a consequence of its ethylene oxide number (EON) distribution, which often follows a Poisson law (4), a commercial surfactant may contain substances with widely different properties; for instance a commercial nonylphenol with an average of 5 EO groups per nonylphenol molecule contains about 50% of substances which are not water soluble. In presence of both an oil and a water phase this can result in an independent solution behavior of each substance. When all the mixture surfactant species do not behave collectively, the low EON ones tend to migrate into the oil phase, i.e., a severe fractionation can

occur. As a consequence the effective surfactant mixture at interface departs considerably from the surfactant mixture which was introduced in the first place in the system (5). This situation is often worsened by a current practice in surfactant handling, i. e., mixing different surfactants in order to attain some average value or some synergistic effect. Such mixing may result in EON distributions with very wide range and two or more modes.

The surfactant users need to know the oligomer composition of alkylphenol nonionics in different phases, generally oil and water, and sometimes a third one, so-called a microemulsion; this knowledge can be processed to calculate the real interfacial surfactant mixture (5-6), an important information since it has been recently found that the physico-chemical conditions at interface are linked with the properties of the associated emulsions (7-10) and foams (11).

ANALYSIS OF ETHOXYLATED ALKYLPHENOLS

Various chromatographic procedures have been tried to separate the commercial ethoxylated alkylphenols into their different oligomers.

Thin layer and paper chromatography (12-15) are limited to qualitative analysis. Gas chromatography (16-21) has been used only for the low average EON mixtures, since it fails to separate higher oligomers ($EON > 8$), because of their low volatility and the thermal degradation that can take place. For these reasons, high performance liquid chromatography (HPLC) appears to be the choice method for the separation and characterization of ethoxylated alkylphenols (22-25).

Ethoxylated monoalkylphenol surfactants have been separated by both reverse and normal phase HPLC. In reverse phase chromatography the separation depends upon the alkyl group in the surfactant molecule and the retention mechanism is governed by hydrophobic interactions between the alkyl tail of the surfactant and the bonded stationary phase; octadecyl or octyl-silane columns have been used for such separations (26-30). However, the alkylate base material is often monoisomeric, and the main analysis problem is to separate the oligomers according to their ethylene oxide number; for such a separation, normal phase chromatography is the logical choice; silica gel (26, 31-32) and silica with chemically bonded nitrile (31, 34), diol (32), and amino phases (23, 24, 30, 35-39) have been tested as column packing in normal phase HPLC separations.

In a recent report, several column packings for normal phase separation were tested with aliphatic alcohols and hydrocarbon solvents (40), in order to compare the chromatographic behavior of underivatized ethoxylated nonylphenols on different stationary phases. A normal phase HPLC separation of ethoxylated nonylphenol oligomers has been described by Zhou et al. (41), who used a silica-diol column and a nonpolar solvent gradient elution. HPLC analysis of oligomer distribution of low EON ethoxylated alkylphenols was selected for interlaboratory testing, using diol bonded phase column under isocratic and gradient conditions (42, 43). In a recent paper (44), we reported that the selection of a proper three-component solvent mixture allows to separate the ethoxylated nonylphenol oligomers up to EON = 12 on a silica column.

In most of the cited reports, detection is carried out by measuring the UV absorbance at a wavelength corresponding to the substituted benzene ring, i. e., at 270-280 nm. It has been shown that the UV absorbance leads to the molar concentration in alkylphenol base and is independent on the EON (24, 37, 45).

This review indicates that HPLC is the choice method to analyze commercial polyethoxylated alkylphenol surfactants, and that there exists a variety of stationary phases and solvent mixtures to do so. However, the previous publications deal with the analysis of a sample of a (single) commercial surfactant, i. e., a mixture with a narrow range single mode EON distribution.

In this paper, we will address the problem of analyzing wide EON distribution mixtures found either in microemulsion systems, or by purposely blending two commercial surfactants, so that a highly bimodal EON distribution is attained. In such a case, the difficulty is to separate oligomers with very different poly-EO chain lengths, ranging from oil soluble to very water soluble, which can be present in very different amounts. The path leading to the optimum column/solvent conditions is discussed.

Additionally, the optimized HPLC separation is applied to the separation of a new commercial surfactant of the same family but with three alkyl groups on the benzene ring : the tri-butyl phenol ethoxylates.

HPLC EQUIPMENT AND EXPERIMENTAL PROCEDURE

HPLC separations are performed on a liquid chromatography equipment consisting of two M6000A pumps and a U6K injector from

Waters Associates, an UV variable wavelength detector model Dupont model 837 operated at 270 nm, and an integrator Varian model 4270.

Whenever it is used, the solvent gradient elution is carried out with a Waters model 660 solvent programmer. All flow rates are set to 1 ml/min.

Two column are used : (1) a silica column, stainless steel, 250 mm x 4.6 mm, Lichrosorb Si 60 - 10 μm , manufactured by Hibar-Merck. (2) an intermediate polarity column, stainless steel, 250 mm x 4.6 mm, Adsorbosphere NH_2 - 10 μm , made by Alltech. The precolumns were filled with the same material than the analytical columns.

Surfactants are analyzed either as received from the manufacturer, or as extracted from a water, oil or microemulsion phase, according to a procedure discussed elsewhere (44). Whatever the origin of the surfactant sample, it is evaporated to dryness and then diluted with methanol down to a concentration in the 0.05 mol per liter range. Aliquots (5 or 10 μl) of these methanol solutions are injected for chromatographic analysis.

N-heptane, chloroform and methanol are HPLC grade solvents from Baker Chemicals. Whenever a gradient elution is carried out solvent A refers to the initial solvent, while solvent B is the secondary one. The solvent mixture composition is indicated on a volume percentage basis.

NPX refers to an ethoxylated nonylphenol oligomer with X ethylene oxide groups per nonylphenol molecule; by extension and for a commercial product, it represents a mixture of ethoxylated nonylphenols with an average of X ethylene oxide group per molecule;

commercial nonylphenols received from Stepan Chemicals (Makon brand) and Hoechst gmbh (Arkopal trade name) were found to exhibit a Poisson distribution with average EON very close to the one claimed by the manufacturer. TBPX stands for tri-butyl phenol ethoxylate, where X is the average number of EO group per molecule; they were received from Hoechst gmbh which manufactures them under the trade name Sapogenat T. The surfactant mixture composition is indicated on a mol percentage basis.

ISOCRATIC HPLC ON A SILICA COLUMN

Isocratic HPLC is the first alternative to be considered because of its attractive features for routine analysis: simplicity, low cost, and rapidity. Such a technique is applied to the separation of oligomers of commercial ethoxylated nonylphenols with different average EON. The silica column tends to retain the different species according to their EON. Thus the solvent must exhibit a low polarity.

The optimization variable is the solvent polarity, which can be changed by mixing different amounts of an apolar solvent (heptane) with a polar one (methanol), together with a third solvent (chloroform) which is added to insure miscibility of the others. A heptane-chloroform-methanol 70-10-20 mixture is found to produce the best compromise between separation and retention, as discussed elsewhere (44). The method is applied to an equimolar mixture of commercial products NP4 + NP10 so that the covered EON spectrum ranges from 1 to 15. Figure 1 (left) shows that the resolution is good up to EON = 10,

but that the retention becomes too severe beyond EON = 12. Actually this method should be the preferred one up to an average EON = 8, i.e., when there is no oligomer with more than 12 EO groups. Above this value, something should be done to reduce the retention time of high EON oligomers.

SOLVENT GRADIENT HPLC ON A SILICA COLUMN

In order to reduce the retention time of high EON oligomers, without affecting the retention time of low EON oligomers, a solvent gradient technique must be used. The column is still the same, but this time the optimization variables are the solvents A and B nature and the mixing programming.

Since the heptane-chloroform-methanol 70-10-20 mixture exhibited the best separation in the isocratic mode, the gradient program is set to scan from a slightly less polar solvent to a slightly more polar solvent.

Base solvent A is a heptane-chloroform-methanol 75-10-15 mixture, which would allow an excellent separation of low EON oligomers. The second solvent B must be more polar, but its mixture with solvent A must not become too polar, because it would elute all high EON oligomers together. Trial and error experiments were carried out on a NP4 + NP10 surfactant mixture, and the best performance was attained with a linear gradient from 0% to 10% of solvent B (chloroform-methanol 50-50), over a 15 minutes period. Figure 1 (right)

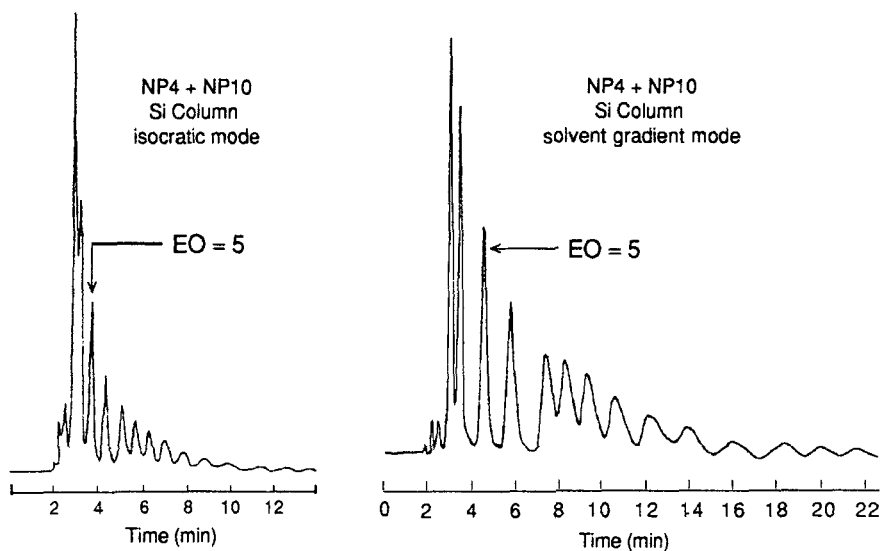


FIGURE 1 : Chromatograms from the analysis of equimolar mixtures of NP4 and NP10 on a silica column. Left : Isocratic mode with heptane-chloroform-methanol 70-10-20. Right : Gradient mode starting with solvent A heptane-chloroform-methanol 75-10-15, and adding solvent B chloroform-methanol 50-50 according to a linear gradient from 0 to 10 % B over 15 minutes.

indicates that the separation is somewhat better than in the isocratic mode, with a better definition and resolution of the peaks in the whole EON range.

However the difference is not that striking and the high EON oligomers are still retained too long a time. It is found that an increase in solvent B polarity or proportion does not improve the performance of the method. It is thus concluded that a less polar column should be

selected, in particular if surfactants with EON higher than 15 are to be analyzed.

ISOCRATIC HPLC ON A NH₂ COLUMN

As in the previous case, the NH₂ column is tested first in isocratic mode in order to optimize the solvent mixture. Since the purpose is to separate higher oligomers, a NP20 commercial surfactant with an EON distribution from 10 to 30 is tested.

Since the column is less polar than the previous one, the appropriate solvent mixture is probably less polar. Figure 2 shows the chromatograms produced with three heptane-chloroform-methanol mixtures, respectively: (a) 80-10-10, (b) 85-5-10, (c) 90-5-5.

Solvent mixture (a) exhibits a quick elution and a poor separation. It is obviously too polar. In mixture (c), half the methanol and half the chloroform have been replaced by heptane, to make up a much less polar solvent. The separation is better than in the previous case (a), but the retention times are much longer. Mixture (b) exhibits an intermediate polarity, and the corresponding chromatogram displays a good compromise between separation and retention time; however it is worth noting that the very low EON species (not present in NP20) might not be well separated. This method is thus satisfactory for ethoxylated nonylphenol with EON ranging from 12 to 28.

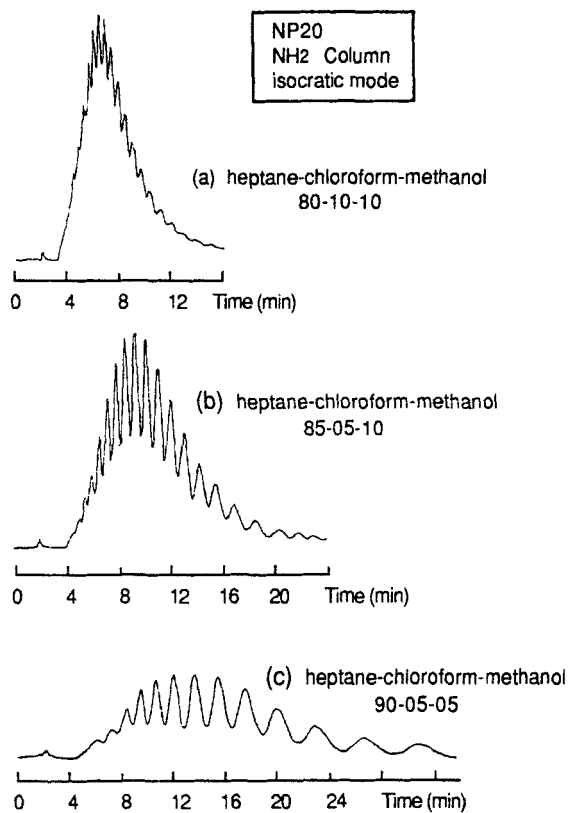


FIGURE 2 : Chromatograms from the analysis of NP20 on a NH₂ column. Isocratic mode with different solvent mixtures.

SOLVENT GRADIENT HPLC ON A NH₂ COLUMN

A wider EON range can be reached by using a solvent gradient. In order to separate the very low EON species first, a slightly less polar solvent is taken as base solvent A (heptane-chloroform-methanol 90-5-5), then it is mixed with a more polar solvent B (chloroform-methanol 50-50) according to a linear program from 0 to 20% of B in 15 minutes.

Figure 3 shows the separation of an equimolar mixture of NP4 + NP10 + NP20 surfactants with an extremely wide range of EON (1 to 28), in the above mentioned conditions. It is seen that the separation is fairly satisfactory over the whole range, altogether with a reasonable retention time. The chromatogram displays the three modes resulting from the superposition of three Poisson distributions, with maxima located at EON = 3, 9 and 18 respectively

APPLICATION TO THE ANALYSIS OF ETHOXYLATED NONYLPHENOL MIXTURES IN MICROEMULSIONS

Such wide range EON distributions are encountered in surfactant fractionation, although the limitations of the GC analytical technique have restricted the studies to low EON mixtures up to now (5-6). Real nonionic surfactant formulations can fairly well contain mixtures of very different products such as NP4 and NP20. These mixtures can exhibit a differential rather than collective behavior at interface; as a consequence, the different oligomers can fractionate between the two or three phases at equilibrium, as discussed elsewhere (46).

The phase behavior of a NPX mixture/water/heptane system is scanned as in previous work (44, 46), but this time by mixing NP4 and NP20, i. e., a very lipophilic surfactant and a very hydrophilic one. As discussed elsewhere (46) there is no three phase microemulsion at optimum formulation, which is located by the minimum in interfacial tension at 91 mol.% NP4 and 9 mol.% NP20. It has been shown that

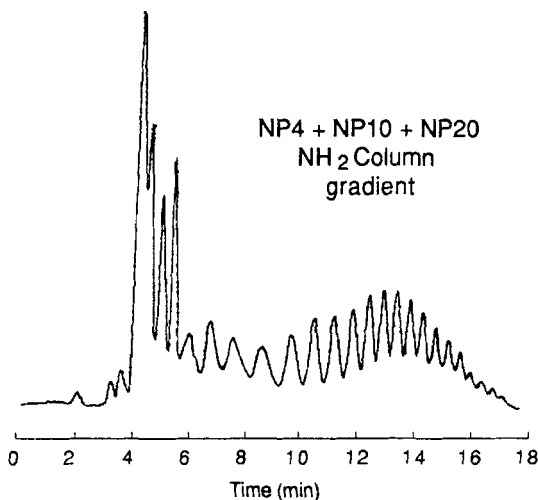


FIGURE 3 : Chromatograms from the analysis of equimolar mixtures of NP4, NP10 and NP20 on a NH_2 column. Gradient mode starting with solvent A heptane-chloroform-methanol 90-5-5, and adding solvent B chloroform-methanol 50-50 according to a linear gradient from 0 to 20 % B over 15 minutes.

adding some amount of NP10 fills the gap between the two distributions and contributes to the formation of a three phase system at optimum : a microemulsion with excess oil and water phases (46). The three phase behavior is found to occur at the following overall composition : 86 mol.% NP4 + 6.2 mol.% NP10 + 7.8 mol.% NP20. The microemulsion, oil and water phases are analyzed according to the previously described procedure (NH_2 column and solvent gradient). Figure 4 shows the resulting chromatograms corresponding to similar surfactant concentrations. Actually 78 mol.% of the total surfactant is

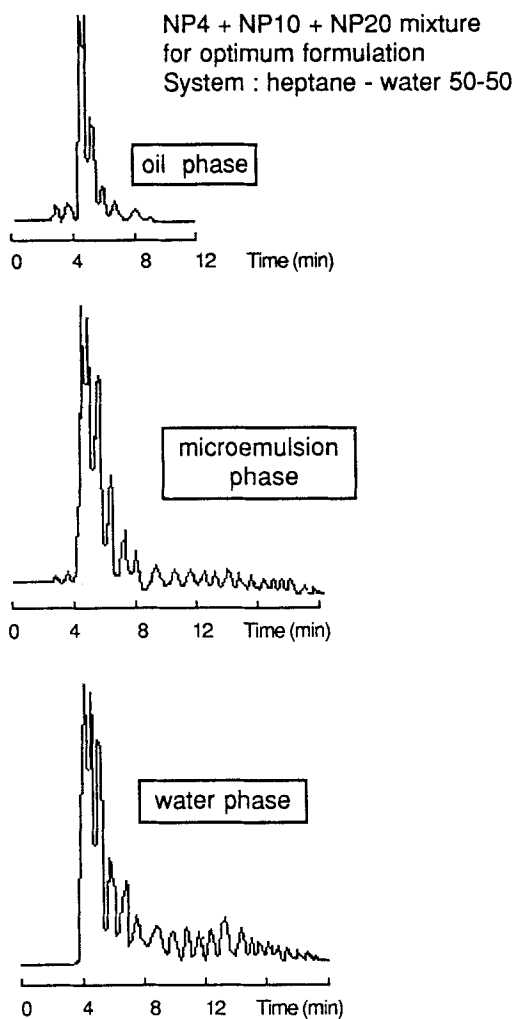


FIGURE 4 : Chromatograms from the analysis of NPX surfactants in the oil, microemulsion and water phases of an optimum three-phase system. Same experimental conditions as in Figure 3.

found in the microemulsion phase, 20 mol.% in the oil phase and only a residual 2 mol.% in the water phase. The data indicates that the oil phase extracts the low EON species, while there are more high EON species in the water phase than in the microemulsion phase, an evidence of the severe fractionation which occurs in such systems.

APPLICATION TO THE ANALYSIS OF ETHOXYLATED TRIBUTYL-PHENOL COMMERCIAL SURFACTANTS.

The gradient technique on NH_2 column is applied to commercial ethoxylated tributyl phenol (TBP) surfactants. Solvent A (heptane-chloroform-methanol 90-5-5) and B (chloroform-methanol 50-50) are the same than previously, but the trial and error optimization leads to a slightly modified program to produce a more polar mixture at the end : linear gradient from 0 to 30% of B in 20 minutes.

The chromatograms of both surfactants shown in figure 5 display an excellent separation of the oligomers. The average EON is found to be respectively 13 and 18, in accordance with the manufacturer data. However, it is worth noting that this sample of TBP13 exhibits a strongly bimodal EON distribution, an indication that it is probably a mixture of substances; if it is assumed that it is composed of two mixtures, each of them with a Poisson EON distribution, a straightforward calculation indicates that these mixtures should contain an average EON of 7 and 14 respectively.

Since the tributylphenol group possesses twelve alkyl carbon atoms, while the nonylphenol has only nine, it might be thought that

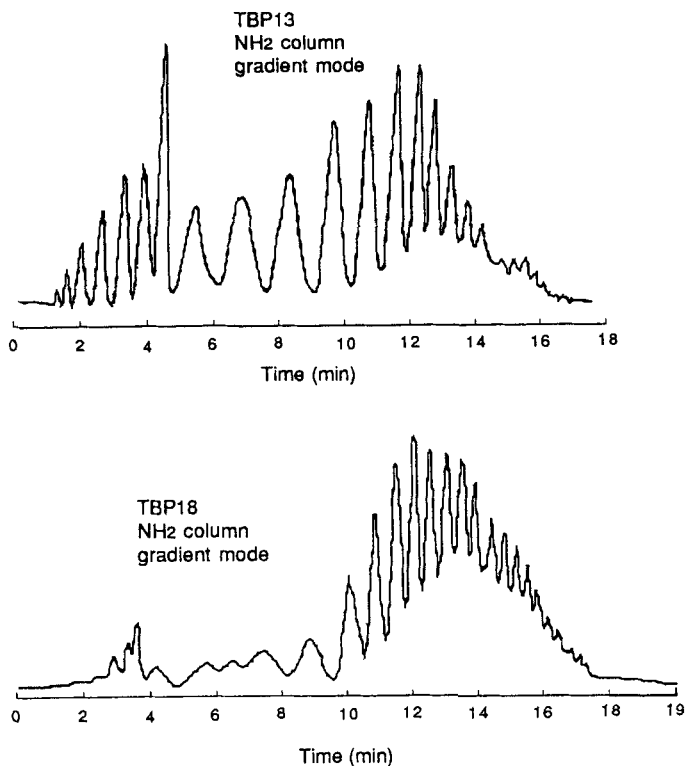


FIGURE 5 : Chromatograms from the analysis of TBP13 and TBP18 on a NH₂ column. Gradient mode starting with solvent A heptane-chloroform-methanol 90-5-5, and adding solvent B chloroform-methanol 50-50 according to a linear gradient from 0 to 30 % B over 20 minutes.

each tributylphenol ethoxylate would be as a whole less polar than its nonylphenol counterpart (with same EON). Figure 5 data indicates the contrary. In effect, the retention time of oligomers with EON = 18 is 14 minutes in both cases, but the solvent mixture is more polar in the TBP18 case than in the NP18 case.

On another hand, if the same solvent gradient is used for both types, the tributylphenol ethoxylate exhibits a longer retention time than the nonylphenol ethoxylate counterpart; this means also that the tributylphenol group is more polar or less apolar than the nonylphenol group, a result which may be attributed to the branching.

The relative polarity of nonionic surfactants is usually measured through their Hydrophilic-Lipophilic Balance, so-called HLB number, which ranges from a few units for hydrophobic substances to 12 and more for hydrophilic ones. HLB was introduced as an empirical parameter by Griffin (47, 48), and later on was correlated with many surfactant properties, as reviewed recently by Becher (49). For monoalkylphenol ethoxylates the HLB number is generally estimated as 1/5 of the weight percentage of ethylene oxide in the molecule (48). Since the tributylphenol group has been found to be less hydrophobic than the nonylphenol group, a coefficient substantially greater than 1/5 is expected to apply in the computation of the HLB of TBPX surfactants. However physico-chemical studies would have to be carried out to know the exact value of this coefficient.

ANALYSIS WITH SILICA AND NH₂ COLUMNS IN SERIES

The previous discussion has shown that the silica column exhibits a good separation of low EON oligomers, while the NH₂ column is well suited for the high EON ones. If they are combined in series it might be possible to take advantage of both features. Of course

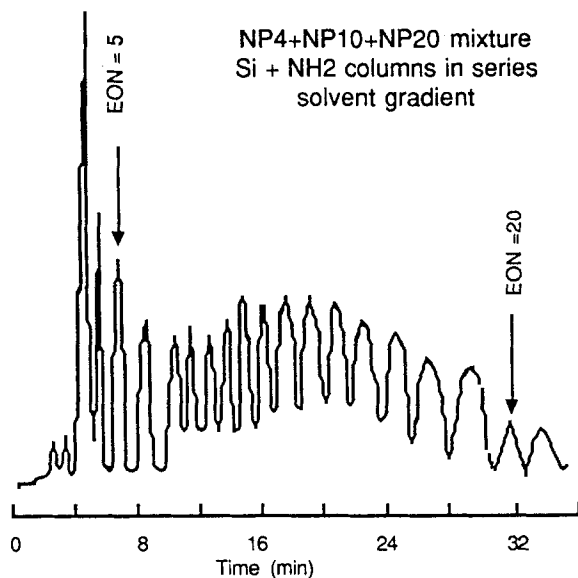


FIGURE 6 : Chromatograms from the analysis of equimolar mixtures of NP4, NP10 and NP20 on Silica-NH₂ columns in series. Gradient mode starting with solvent A heptane-chloroform-methanol 70-15-15, and adding solvent B chloroform-methanol 25-75 according to a linear gradient from 0 to 40 % B over 25 minutes.

the solvent would have to be adapted to each column separation through an appropriate program.

The silica and NH₂ columns are placed in series, and several solvent mixtures are tested to separate an equimolar NP4 + NP10 + NP20 mixture. A polar solvent made of chloroform and methanol (from 25-75 to 75-25) is tested first, with poor results. Then a ternary solvent (heptane-chloroform-methanol) is tested, with the better separation reached with 70-20-10 and 70-15-15 mixtures, but with very

long retention times. In order to reduce the retention time, solvent B should be selected as more polar than in previous experiments.

Gradient elution is optimized by varying solvents A and B and manipulating their mixing program. The best separation is attained in the following conditions : solvent A heptane-chloroform-methanol 70-15-15; solvent B chloroform-methanol 25-75; gradient program from 0% to 40% B in 25 minutes.

Figure 6 shows the separation of the wide EON range mixture in these conditions. The chromatogram displays an excellent separation of the peaks, either at low or high EON, which makes the technique an attractive candidate for preparative separation purposes.

It is worth noting that an even better separation can be attained by mixing a lesser amount of solvent B, although it requires a retention time beyond 45 minutes, which is considered excessive for practical purpose.

CONCLUSIONS

Low EON oligomers ($EON < 8$) of ethoxylated alkyl phenol surfactants are easily separated on a silica column with an appropriate mixed solvent; the use of solvent gradient programming allows to increase the limit up to $EON = 15$ on a silica column.

Higher oligomers are separated better by using a NH_2 column, either by isocratic elution or solvent gradient programming. The technique can be applied to the analysis of wide EON distribution (1 to

28) in complex systems such as microemulsions. It also allows the separation of the ethoxylated tributyl phenol oligomers in a commercial surfactant.

Finally, by using two columns (Si and NH₂) in series, with a proper solvent gradient programming, an even better separation method is attained, which may be the choice method for preparative separation.

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